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VITRIFICATION, PROPERTIES, AND STRUCTURE OF LEAD-TELLURITE BORATE GLASSES

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The vitrification, structure, and physicochemical properties of glasses in the $PbO – ZnO – B_2O_3 – TeO_2$ system are studied. The dual role of the lead ions in the glass structure is confirmed. It is demonstrated that the co-ordination transition of boron ions correlates with the concentration of PbO in glass. A nonlinear dependence of properties on the glass composition is due to the structural modifications in glass.

The lead-tellurite boron-containing system $PbO – ZnO – B_2O_3 – TeO_2$ serves as the basis for synthesis of low-melting glasses used in sealing and passivation of electronic instruments and devices. The high fusibility of glasses in this system is determined by its main components: lead, tellurium, and zinc oxides. Compounds containing cations with an outer electron shell of 18 (Zn^{2+}) and 18 + 2 (Pb^{2+}, Bi^{3+}, Tl^{3+}, As^{3+}, Te^{4+}, and Sb^{3+}) electrons have the highest capacity for lowering the melting temperature of a material [1]. Owing to the high degree of polarization of these cations, the optimum screening of positive nuclei by electrons or anions is provided, which leads to a decreased melting temperature of the material. Thus, lead, tellurium, and zinc oxides containing highly polarizable cations and ensuring low temperatures of softening, fusion and, accordingly, sealing are necessary components in developing low-melting solder glasses.

The interest in glasses of the specified system is primarily due to the fact that in addition to the classical glass-forming agent (boric anhydride) they contain oxides of heavy metals (zinc and tellurium) that can act as glass-forming agents in the glass structure.

The purpose of the present study was to investigate the glass formation, properties, and structural specifics of glass in the $PbO – ZnO – B_2O_3 – TeO_2$ system. We have investigated the low-boron composition range with a constant content of B_2O_3 equal to 10% (here and elsewhere molar content indicated).

Glasses were melted in corundise crucibles of 50 ml capacity at a temperature of $900 \pm 50°C$ in a Silit electric furnace. The initial materials included boric acid, red lead, and tellurium and zinc oxides.

The vitrification diagram is shown in Fig. 1. The area of glass-forming compositions is located along the $PbO – TeO_2$

side of the Gibbs concentration triangle and is limited by the following component content (%): 10 – 70 PbO, 10 – 20 ZnO, 10 – 70 TeO_2. Two areas of glass-forming compositions can be distinguished in Fig. 1: the high-lead and the high-tellurium areas.

The color of the glasses synthesized varies from light yellow to light green depending on the respective content of lead oxide and tellurium oxide.

The boundaries of the ranges of noncrystallizing clear glasses and glasses crystallizing under thermal treatment are identified, which makes it possible to predict the composition of clear glass solders and of glass ceramic cement. The range of glasses not crystallizing in heat treatment increases
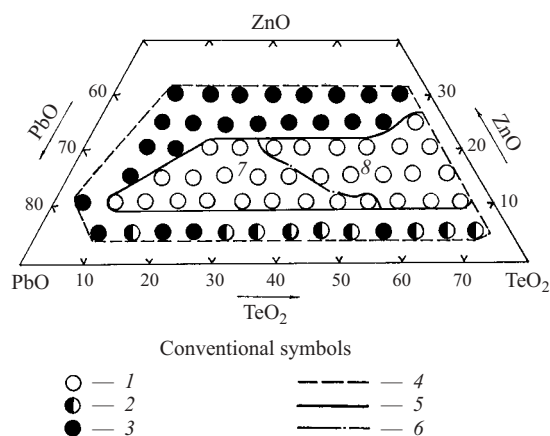

Fig. 1. Diagram of vitrification and crystallization of glasses in $PbO – ZnO – B_2O_3 – TeO_2$ system: *1*) glass; *2*) glass with unmelted portions; *3*) crystallized melt; *4*) area of investigated compositions; *5*) area of vitrification at 950°C; *6*) phase boundary of crystallizing and non-crystallizing glasses; *7*) crystallizing glass area; *8*) non-crystallizing glass area.

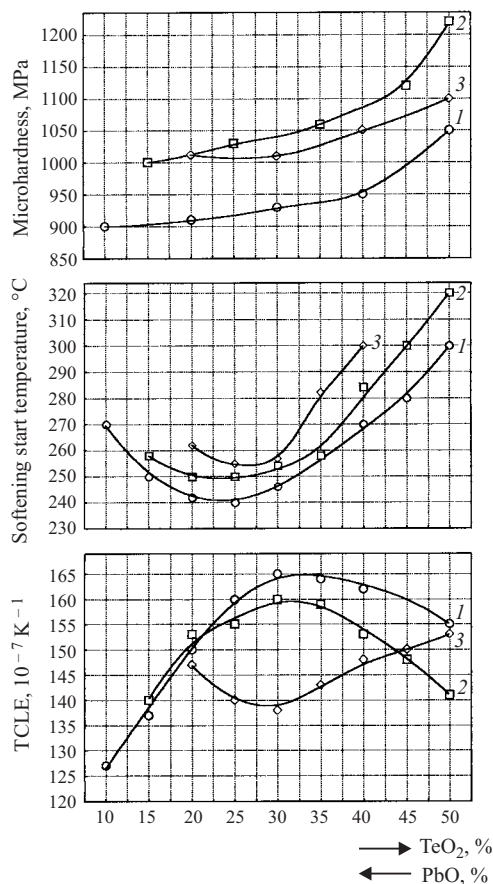[1] Belarus State Technological University, Minsk, Belarus.

Fig. 2. Dependence of glass properties on their composition with the ZnO content equal to 10% (*1*), 15% (*2*), and 20% (*3*).

as the ZnO content increases and is shifted toward the low-zinc compositions. High-lead glasses are inclined to crystallization. It is observed that high-tellurium glasses exhibit a stable vitreous state.

From the engineering point of view, the most interesting are compositions containing up to 50% TeO_2. Glasses with a TeO_2 content above the specified level are not suitable for technological use and instantly crack in production.

The lead and tellurium content in the synthesized glasses varies over a large interval from 10 to 70%. A high content of lead and tellurium oxides indicates their participation as glass-forming components in the structural lattice of glass.

According to the Stenworth criterion, tellurium oxide is a "conditional glass-former" and forms glasses only in combination with other oxides [2]. The role of the tellurium ion as a glass-former in constructing the structural lattice of lead-tellurite borosilicate glass was mentioned previously [3]. A high concentration of TeO_2 in the considered glass compositions corroborates its glass-forming capacity.

The positive effect of PbO on the glass-forming process is due to the origin of a covalent bond Pb – O, as a result of high polarization of the lead ion determined by the structure of its outer electron shell [4]. According to the NMR data [5], the Pb – O chemical bond in lead-borate glass within the

range of low concentrations of PbO is predominantly ionic. As the PbO content grows, the covalent component in the Pb – O bond increases, and the lead ion is present in the glass in the form of [PbO_4] groups. The authors in [6] established that the concentration threshold, after which the lead ion acts as a glass-former ranges from 20 to 50% PbO both for lead-borate and lead-silicate glasses. A similar behavior of PbO is observed in lead borosilicate glasses [7].

A study of the physicochemical properties demonstrated that the dependence of the properties of glass on its chemical composition is not linear. There are inflections in the curves (Fig. 2) determined by the structural modifications in glass, probably, coordination modifications. In the equimolecular replacement of PbO with TeO_2 in a glass series with a constant content of ZnO equal to 10, 15, and 20%, the extremum points on the concentration dependence curves of the softening temperature and the TCLE correlate with 45 – 50% lead oxide. An increase in microhardness of glass is observed under the same concentrations. This is presumably a concentration threshold, after which the coordination state of the lead ion changes and its dual role is manifested in the structure of the experimental glasses.

It should be noted that when the TeO_2 content in glasses containing 10 – 15% ZnO and the PbO content decreases, first, the TCLE first exhibits a growth then declines, whereas glasses with 20% ZnO demonstrate an opposite course of the curve. The softening temperature for the glasses of this series varies similarly to the TCLE: it first decreases and later increases. However, in both cases the extremum points correlate with the PbO content of 45 – 50% (30% TeO_2). This relationship between the TCLE and the softening temperature is typical only of zinc-bearing glasses. They are the only glasses in which the softening temperature and the TCLE decrease as the ZnO content increases at the expense of PbO and B_2O_3 [4].

The density of the considered glasses grows with the lead oxide content and ranges within the limit of 5900 – 7500 kg/m³. In the equimolar replacement of PbO with TeO_2, the glass density decreases, since tellurium has a smaller atomic mass compared with lead. The strong effect of PbO on increasing the glass density is due not only to the high atomic mass of lead but also to the maximally dense atomic packing developed due to the capacity of lead ions to strongly polarize the nearby oxygen atoms causing compression of cavities, in which the oxygen atoms exist [8].

A study of the structural specifics of glasses in the PbO – ZnO – B_2O_3 – TeO_2 system by infrared spectroscopy indirectly corroborated our assumption of the dual structural role of lead. Figure 3 shows the IR absorption spectra of glasses with a constant ZnO content equal to 10%. The spectra of glasses with a high lead oxide content (50 – 70%) have a wide absorption band with maxima at 1230 and 1180 – 1160 cm⁻¹, weakly resolved bands in the range of 920 and 710 cm⁻¹, and absorption bands at 660 and 475 cm⁻¹. The absorption bands at 1230 and 710 cm⁻¹ are typical of triago-

nally coordinated boron [BO_3] in boroxol rings. The absorption maximum at 1180 cm^{-1} characterizes the chain links of [BO_3] triangles. As both bands have an equal intensity, it can be assumed that the fragments of [BO_3] groups are present in glass both in boroxol rings and in chain structures.

At the same time, absorption bands with maxima at 1050 and 1080 cm^{-1} typical of four-coordination boron [BO_4] are registered, i.e., a coordination transition of boron ions [BO_3] $\rightleftarrows$ [BO_4] is observed, which correlates with a variation in the lead oxide concentration in the glass. It can be assumed that with a 10 – 50% content of PbO, the lead ions acting as modifiers have a high coordination number of 6 in [PbO_6] groups and, as a consequence of the donor-acceptor interaction with boron ions, facilitate a partial transformation of trigonal-coordination boron into the tetrahedral coordination. When the PbO content is above 50%, the coordination state of the lead ions changes to 4, the strength of their bond with oxygen grows, and the lead ions cease to be donors for oxygen. As a consequence, three-coordination boron is formed and accumulated. The intensity of the absorption bands typical of [BO_3] groups increases. The lead in this case acts as a glass-forming agent and is incorporated in the glass lattice in the form of [PbO_4] tetrahedra. The transition of lead ions from one structural state to another is manifested in the inflections in the curves indicating the dependence of glass properties on the composition.

The absorption band with maxima at 660 cm^{-1} is determined by the tellurium-oxygen groups. As the Te$_2$O content grows from 10 to 60%, the position of this band does not vary. Only with a TeO$_2$ content equal to 70% is the absorption band maximum shifted towards the high-frequency spectrum range up to 690 cm^{-1}.

The structure pattern of tellurium-containing glasses is determined by trigonal pyramids [TeO_3] and bipyramids [TeO_4], whose unusual structure causes the emergence of an intermediate coordination state of tellurium ions: $3 + 1$ [9, 10]. The absorption in the range of $600 – 700$ cm^{-1} in such glasses is determined by the valence vibrations of Te – O bonds in [TeO_3] and [TeO_4] groups. The absorption of [TeO_3] groups has a higher-frequency position than [TeO_4] groups; however, this difference is insignificant due to the manifestation of the intermediate coordination state of tellurium ion: $3 + 1$. In the general case, the absorption band range of [TeO_3] groups correlates with frequencies of $650 – 700$ cm^{-1}, and that of [TeO_4] groups correlates with $600 – 650$ cm^{-1}.

Analyzing the obtained results and comparing them to the published data, one can assume the presence of trigonal pyramids [TeO_3] in the structure of the experimental glass. The absorption band stability in this case indicates that the coordination state of tellurium ions in glass does not change at any concentration. The slight shift of the absorption band toward the short-wave range can be a consequence of increased degree of polymerization of the tellurite glass lattice.
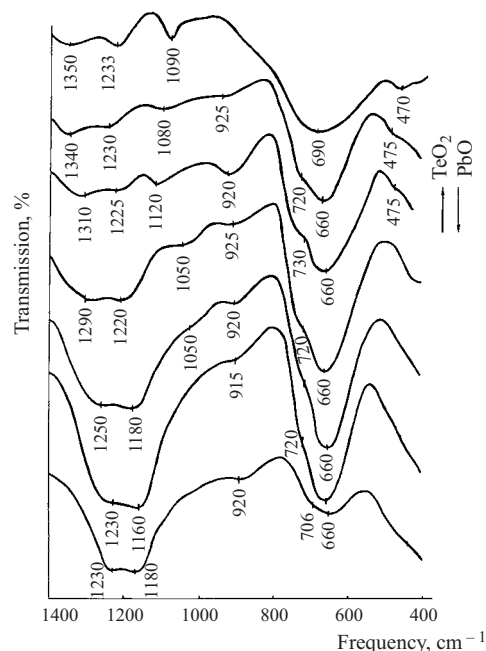

Fig. 3. IR absorption spectra of glasses in equimolar replacement of PbO with TeO$_2$ (10% ZnO).

The absorption band at 475 cm^{-1} can probably be attributed to [ZnO_4] groups.

Since the considered glasses contain a set of different structural groups, it is very difficult to properly interpret their structure. One can only assume that the basis of this glass is a lead-tellurium lattice with certain fragments of the borate component. Depending on the concentration of the lead and tellurium oxides in glass, the lead or the tellurium basis will prevail. One cannot exclude the incorporation of four-coordination zinc ions in the structural lattice of glass.

The electron-microscope studies established the microheterogeneous structure of these glasses. The microheterogeneities in glass are of the liquation origin. As the TeO$_2$ concentration in glasses with 50% PbO grows at the expense of ZnO, the structure changes from a droplet structure, on whose background large isolated spheroid and ellipsoid stratification areas of size $0.5 – 1.0$ μm are visible, to a maze-like structure and then to an interpenetrating structure (Fig. 4). A good reason for the origin of liquation in the considered glasses is the presence of more than one glass-forming component (B$_2$O$_3$, TeO$_2$) under certain concentrations of PbO. This leads to the formation of locally isolated microgroups, which are the source of liquation microstratification.

The study performed clarified the structural specifics of lead-tellurium borate glasses and confirmed the dual structural role of lead ions. It is established that a modification of the structural state of lead ions correlates with the coordination transitions of boron ions. The tellurium ions under any concentration of TeO$_2$ in glass do not change their coordination state and are present in the glass structure in the form of trigonal pyramids [TeO_3]. The glass properties are non-

Fig. 4. Microstructure of glasses with a constant content of PbO equal to 50% and a TeO$_2$ content equal to 20% (*a*), 25% (*b*), and 30% (*c*).

linearly dependent on their chemical compositions, which is determined by the structural modifications in glasses, namely, a modification of the structural state of the lead ions. The synthesized glasses typically have a liquation structure.

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